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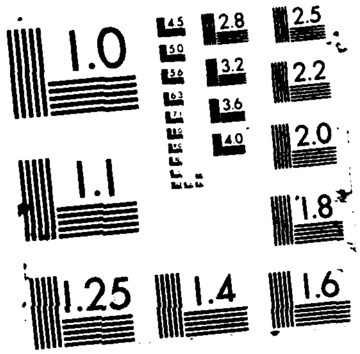
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External Magnetic Field Effects on the Excited States Iridium(I) and Rhodium(I) Complexes

by

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External Magnetic Field Effects on the Excited States of Iridium(I) and Rhodium(I) Complexes*

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Luminescences and excited state lifetimes have been measured for four Ir(I) and Rh(I) complexes at 4 K as a function of magnetic field strength. Induced spectra exhibit a B^2 dependence while the lifetimes are a function of B^{-2}.

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1. Introduction

In 1984 Bär and Gliemann [1] reported a large red-shift (~300 cm^{-1}) of the emission maximum observed from single crystals of $Ba_2Pt_2(H_2P_2O_5)_4$, a $5d^8$ binuclear complex, when an external magnetic field (4 Tesla) was applied. Later, Crosby and coworkers [2] produced an effect of comparable magnitude (~400 cm^{-1}) on the emission of $Ir(I)(2{=}phos)_2ClO_4$ [3] with an external magnetic field. These results are particularly interesting because the observed spectral changes caused by the applied magnetic fields are two orders of magnitude larger than the Zeeman splittings typically observed. The current study was undertaken in order to find more examples of systems that exhibit large magnetically-induced spectral changes and to develop a quantitative model of the low-lying excited states of these nd^8 metal complexes.

Many compounds of the type $M(P\text{-}P)_2ClO_4$ [4] have been investigated optically. Moreover, both the steady state and the transient luminescence properties of these cations signify an energy-level scheme consisting of an emitting triplet term split by spin-orbit coupling into a lower highly forbidden level and a degenerate pair that is formally allowed and lies ~100 cm^{-1} above the forbidden one. Such a disposition of levels is optimal for observing magnetic perturbations of the luminescence, and our investigations have thus focused on systems of this type, particularly those analogous to Ir(I)(2=phos)$_2$ClO$_4$.

2. Experimental

The chlorides of the complexes were prepared by published procedures [5,6] and subsequently metathesized to the perchlorate salts by the method of Geoffrey et al. [7]. Optical measurements were carried out with a Janis Model RD cryostat equipped with an American Magnetics superconducting magnet capable of producing field strengths of 5 Tesla at the sample position. Steady state excitation was provided by an Osram 200-watt high-pressure Hg lamp, whose output was first passed through 5 cm of a saturated solution of $CuSO_4$ and then through a Corning 7-60 glass UV filter. Microcrystalline samples were affixed with silicone grease or mineral oil to a 7.5-mm diameter copper block. Temperature control was provided by a Lakeshore Cryotronics Model DRC-80C temperature controller with a Ga-As diode sensor. The response of the diode shifted approximately 0.1 K as the field was varied from 0-5 Tesla. Emission from the sample was dispersed through a Spex Minimate monochromator and detected with a RCA 7102 photomultiplier. The experiments were controlled by a Digital Equipment Corporation 11/23 minicomputer that also stored the spectral data. Since the correction factors for the system are essentially constant over the energy range used, all emissions are reported uncorrected. For the transient decay time measurements excitation was provided by a Molectron Model UV22 N_2 laser with a pulse width of 10 ns. The detection system was the same as that for steady state emission, but the phototube signal was amplified and fed into a Biomation Model 6500 waveform recorder. All lifetimes were measured at ~4 K.

To observe any effect of the ambient magnetic field upon the detection system the Hg lamp output was mechanically chopped at approximately 300 Hz and a small fraction of the scattered light directed into the phototube. The geometry of chopper produced a tube response that fell to <10% of the maximum value in less than 1 ms at zero field. When the field was raised to five Tesla both the shape and amplitude of the response were indistinguishable from those at zero field.

Resolution of the total band envelope at each field strength into two components (fig. 2) was achieved by subtracting a percentage of the zero-field spectrum of each complex from the various high-field spectra. This percentage was determined in each case by calculating the ratio of the intensity of the high-field spectrum to the zero-field spectrum at a point on the low energy edge of the band where the contribution from the high field component at zero field could be assumed to be negligible.

3. Results

In fig. 1 the field dependent steady state emission spectra at 4.2 K are shown for the four complexes. The zero-field emission maximum for Rh(I)(diphos)$_2$ClO$_4$ occurs at 634 nm, steps in a regular fashion to higher energy as the field is increased, and maximizes at 622 nm at 4.5 Tesla. A similar result is observed for Rh(I)(2=phos)$_2$ClO$_4$; the zero field maximum lies at 620 nm, but the maximum occurs at 610 nm for 4.5 Tesla. Neither bandshape changes appreciably during this process.

For the Ir(I) complexes, however, the bandshapes do display appreciable field dependence. The emission of Ir(I)(dpbe)$_2$ClO$_4$ maximizes at 579 nm at zero field, with a small shoulder on the high energy side. As the field is increased, the shoulder increases in intensity relative to the maximum, becoming nearly as intense at 5 Tesla as the principal component. The result for Ir(I)(diphos)$_2$ClO$_4$ is similar but less dramatic. The zero-field maximum occurs at 585 nm and two high energy shoulders appear at approximately 565 nm and 572 nm. The Ir(I)(diphos)$_2$ClO$_4$ spectra were recorded at 10 K, but since the populations of the emitting levels are separated by greater than 100 cm^{-1} [8], this temperature difference should not significantly affect the results.

In an attempt to observe the magnetically-induced portion of the emission directly, a subtraction technique was employed to plot induced spectra (see Experimental).

Figure 2 contains the results. The induced spectra from all the compounds are similar; the single exception is that of Ir(I)(diphos)$_2$ClO$_4$, which appears to have two induced bands. As can be seen from fig. 3, the integrated intensities of these induced spectra are proportional to the square of the field strength.

Figure 4 displays the inverse of the emission lifetime plotted against the square of the field strength for each compound. These plots yield fairly linear relationships in each case. The magnitude of the lifetime shortening ranges from a factor of 1.8 to almost 5.

4. Discussion

These Rh(I) and Ir(I) complexes contain d^8 metal centers surrounded by a ligand field that is satisfactorily described by D_{4h} microsymmetry. If we assume the commonly accepted order of the d orbitals in square planar d^8 complexes [7,9], the lowest energy transition should therefore be $(n+1)p_z \leftarrow nd_{z^2}$. This excited configuration leads to $^{1,3}A_{2u}$ terms, with the triplet term split into E_u and A_{1u} sublevels. The high temperature spectrum is believed to be dominated by emission from the higher E_u (x,y-allowed) sublevel, whereas the low temperature emission originates from the A_{1u} component combining with some vibrational mode of the ground state [10]. As an external magnetic field is applied at low temperatures, both intensity and lifetime data indicate that the electronic transitions producing the emission become more allowed. This is readily explained through a mechanism involving field-induced mixing of the formally forbidden A_{1u} state with some higher allowed states. Although it is tempting to infer that the A_{1u} level borrows intensity from the nearby E_u level under the influence of the applied field, data on binuclear rhodium(I) complexes lead us to conclude that the magnitude of spin-orbit coupling is the controlling factor and not the proximity of the formally interacting levels. Thus, we posit a field-induced mixing mechanism that connects the A_{1u} level with a high-lying symmetry-allowed singlet(s).

One issue that must be addressed is the problem of molecular orientation with respect to the magnetic field. Unlike studies of single crystals where the orientation of the complexes relative to the field is often known, microcrystalline samples contain a random distribution of orientations relative to the field. For a D_{4h} complex, the two limiting cases are $H \parallel C_4$ and $H \perp C_4$. For the $Pt_2(H_2P_2O_5)_4^{4-}$ ion Gliemann and coworkers demonstrated that the $H \perp C_4$ geometry produces a much larger effect than $H \parallel C_4$ [1], in accord with preliminary theoretical work in this laboratory. We therefore examine the correlation diagram as an $H \perp C_4$ field is applied and will not further discuss the orientation problem at this time.

The correlation diagram for pseudo D_{4h} d^8 mononuclear metal complexes under the influence of a magnetic field (fig. 5) indicates that under the reduced symmetry of the field ($H \perp C_4$) the lowest A_u can formally interact with the A_u component from the E_u, only ~100 cm^{-1} away. As mentioned above, however, a series of Rh(I) binuclear species with spin-orbit splittings of only 7-10 cm^{-1} failed to exhibit any observable magnetic effects, even at temperatures as low as 1.8 K and under fields of 5 Tesla. From these results we infer that the intrinsic magnitude of spin-orbit coupling is the deciding factor for observing large magnetically-induced spectral changes in these molecules and not the proximity of the levels.

Finally, the linear dependence of the induced emission intensity with the square of the field strength indicates that first-order perturbation theory can adequately describe the mixing of states. This conclusion is further re-enforced by the lifetime data; the total rate constant for decay (τ^{-1}) varies linearly with the square of the field.

References

[1] L. Bär and G. Gliemann, Chem. Phys. Letters 108 (1984) 14.

[2] T. J. Johnson, S. D. Phillips and G. A. Crosby, Chem. Phys. Letters 114 (1985) 388.

[3] (2=phos) is cis-1,2-bis(diphenylphosphino)ethylene.

[4] M = Rh(I),Ir(I); (P-P) = cis-1,2-bis(diphenylphosphino)ethane (diphos) or cis-1,2-bis(diphenylphosphino)ethylene (2=phos) or cis-1,2-bis(diphenylphosphino)benzene (dpbe).

[5] J. P. Collman, C. T. Sears, Jr. and M. Kubota, Inorg. Syn. 11 (1968) 101.

[6] L. S. Chen, Ph.D. dissertation, Pottsdam, New York (1973).

[7] G. L. Geoffrey, M. S. Wrighton, G. S. Hammond and H. B. Gray, J. Am. Chem. Soc. 96 (1974) 3105.

[8] W. A. Fordyce and G. A. Crosby, Inorganic Chem. 21 (1982) 1455.

[9] S. J. Milder, D. S. Kliger, L. G. Butler and H. B. Gray, J. Phys. Chem. 90 (1986) 5567.

[10] W. A. Fordyce, H. Rau, M. L. Stone and G. A. Crosby, Chem. Phys. Letters 77 (1981) 405.

FIGURE CAPTIONS

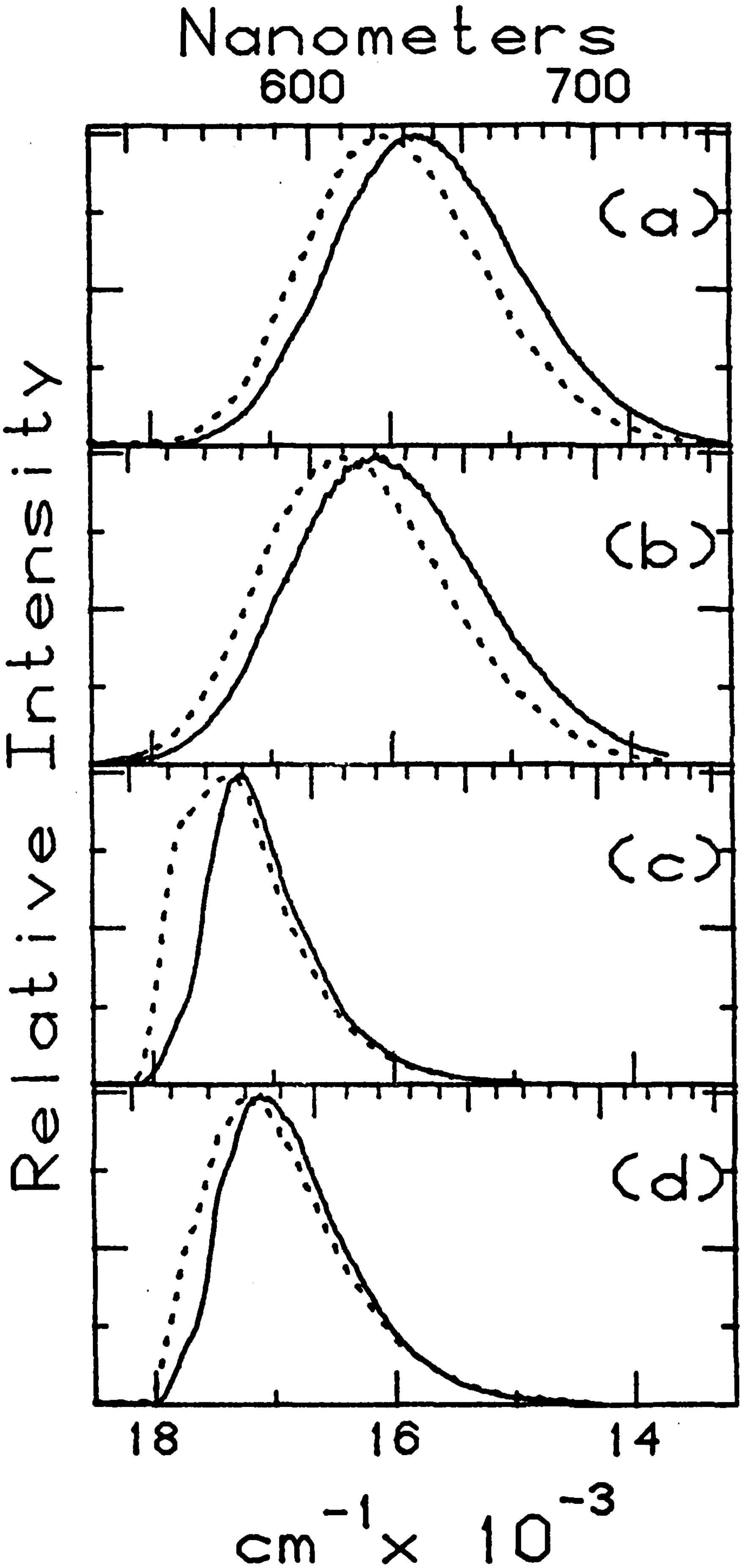
Fig. 1. Steady state emission spectra of solids at field strengths of B = 0 Tesla (- - -) and B = B_{max} (———) at 4.2 K for (a) Rh(diphos)$_2$ClO$_4$ (B_{max} = 4 Tesla); (b) Rh(2=phos)$_2$ClO$_4$ (B_{max} = 4.5 Tesla); (c) Ir(dpbe)$_2$ClO$_4$ (B_{max} = 5 Tesla); (d) Ir(diphos)$_2$ClO$_4$ (B_{max} = 4 Tesla).

Fig. 2. Induced components of the steady state emission spectra of solids at field strengths of 1 Tesla (•••••), 2 Tesla (- - -), and 4 Tesla (———) at 4.2 K for (a) Rh(diphos)$_2$ClO$_4$; (b) Rh(2=phos)$_2$ClO$_4$; (c) Ir(diphos)$_2$ClO$_4$.

Fig. 3. Additional emission intensity as a function of the square of the field strength for Rh(diphos)$_2$ClO$_4$ (▣), Rh(2=phos)$_2$ClO$_4$ (◆), and Ir(dpbe)$_2$ClO$_4$ (■) solids at 4.2 K.

Fig. 4. Inverse of emission lifetime as a function of the square of the field strength for Rh(diphos)$_2$ClO$_4$ (▣), Rh(2=phos)$_2$ClO$_4$ (◆), Ir(dpbe)$_2$ClO$_4$ (■), and Ir(diphos)$_2$ClO$_4$ (◈) solids at 4.2 K.

Fig. 5. Schematic state diagram for a pseudo D_{4h} mononuclear nd^8 metal complex under the influence of spin-orbit coupling and an external magnetic field oriented perpendicular to the C_4 axis. Dashed lines indicate possible interactions under the reduced symmetry imposed by the magnetic field.



Nanometers
600
700
Relative Intensity
(a)
(b)
(c)
(d)
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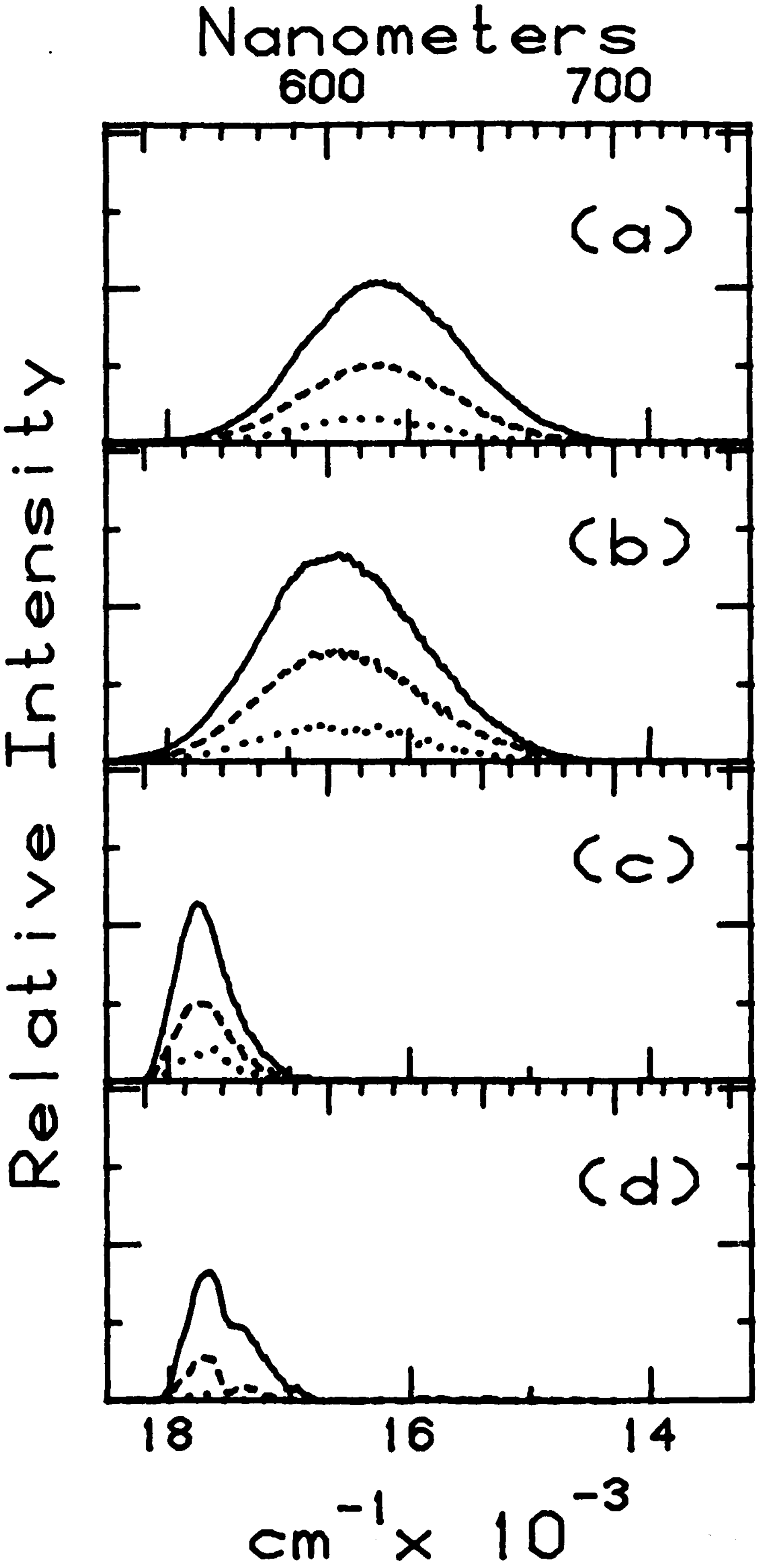
cm^{-1} x 10^{-3}

Fig. 1


Nanometers
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700
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(d)
Relative Intensity
18
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Fig 2

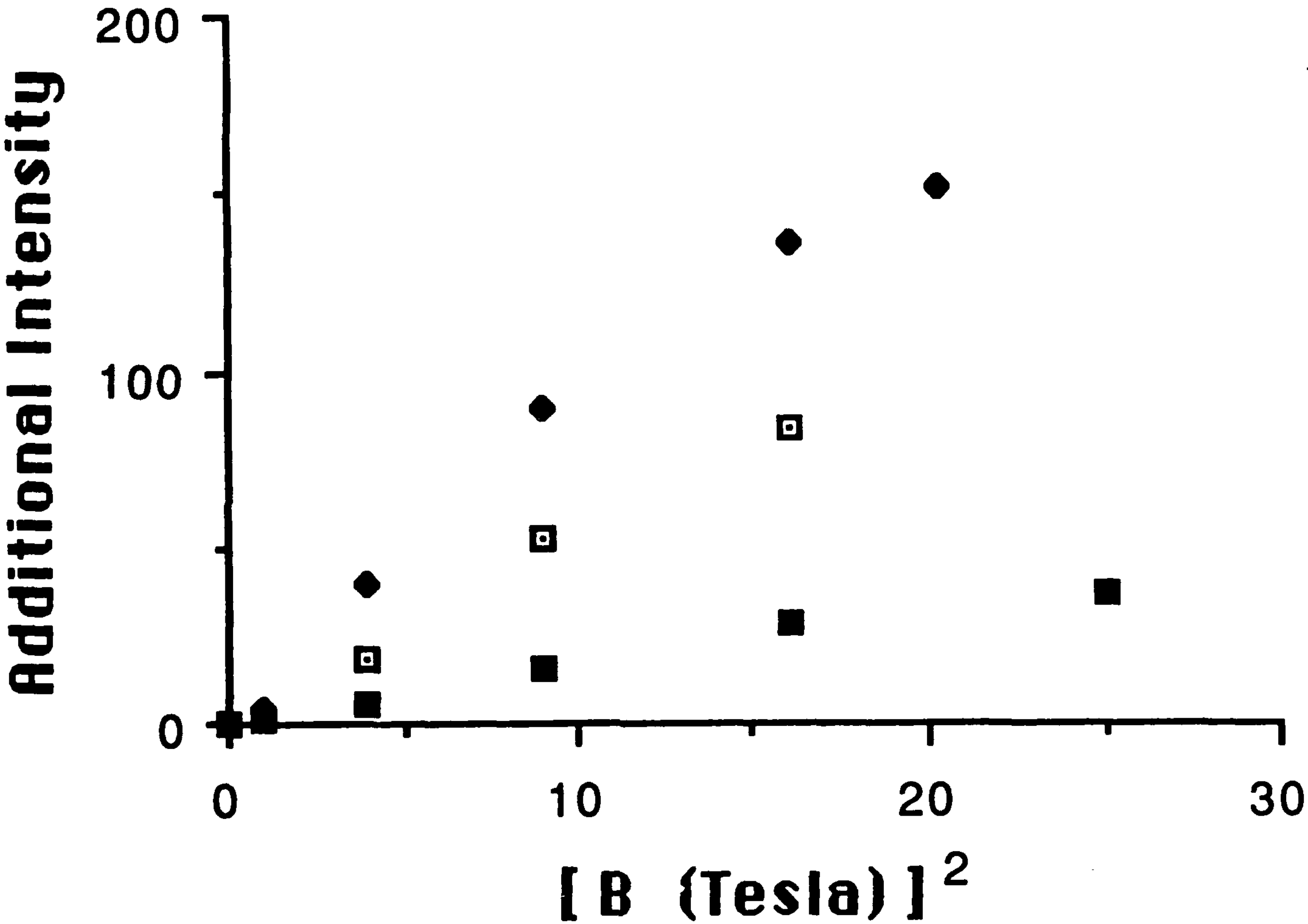


Fig 3

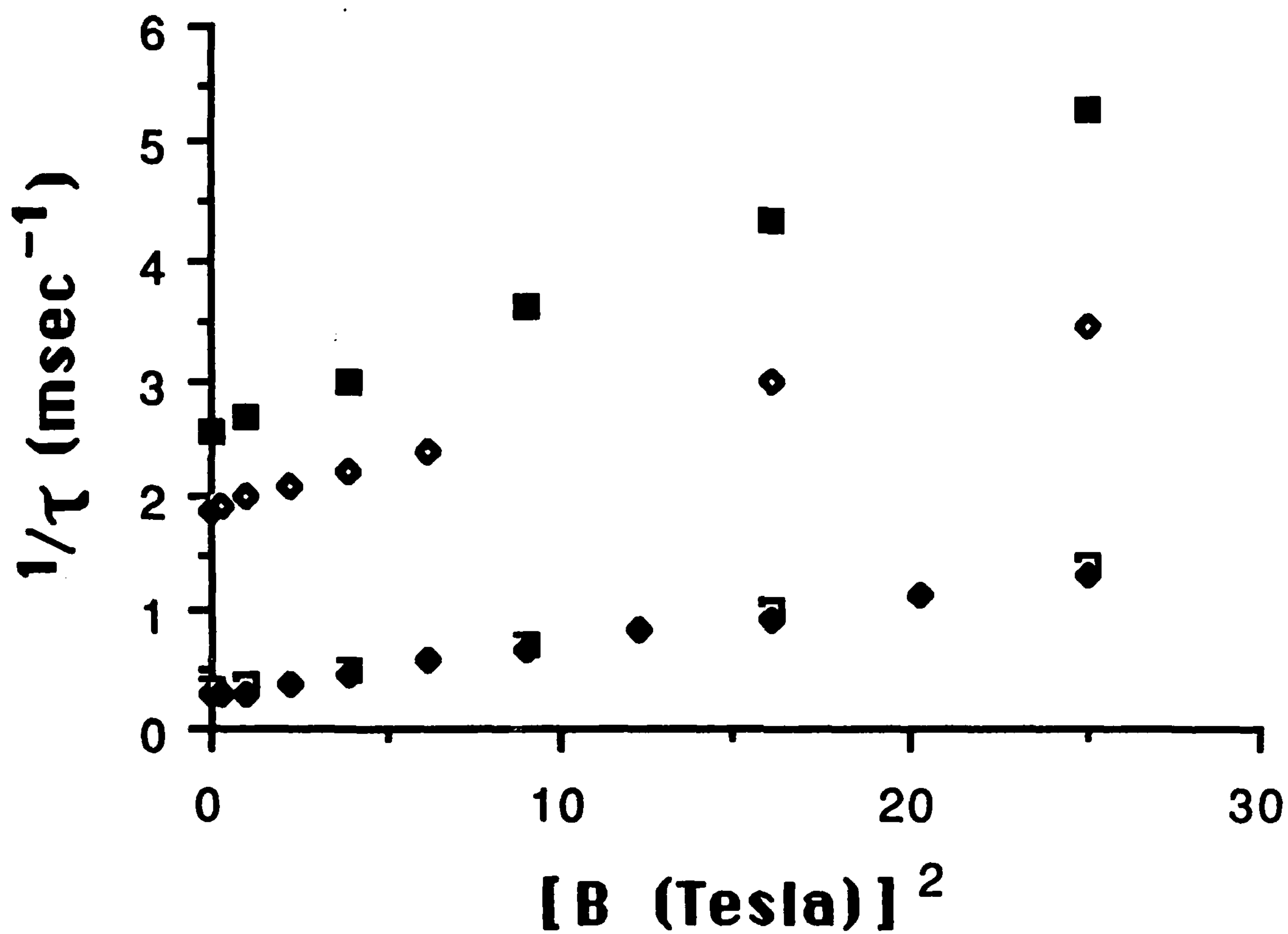
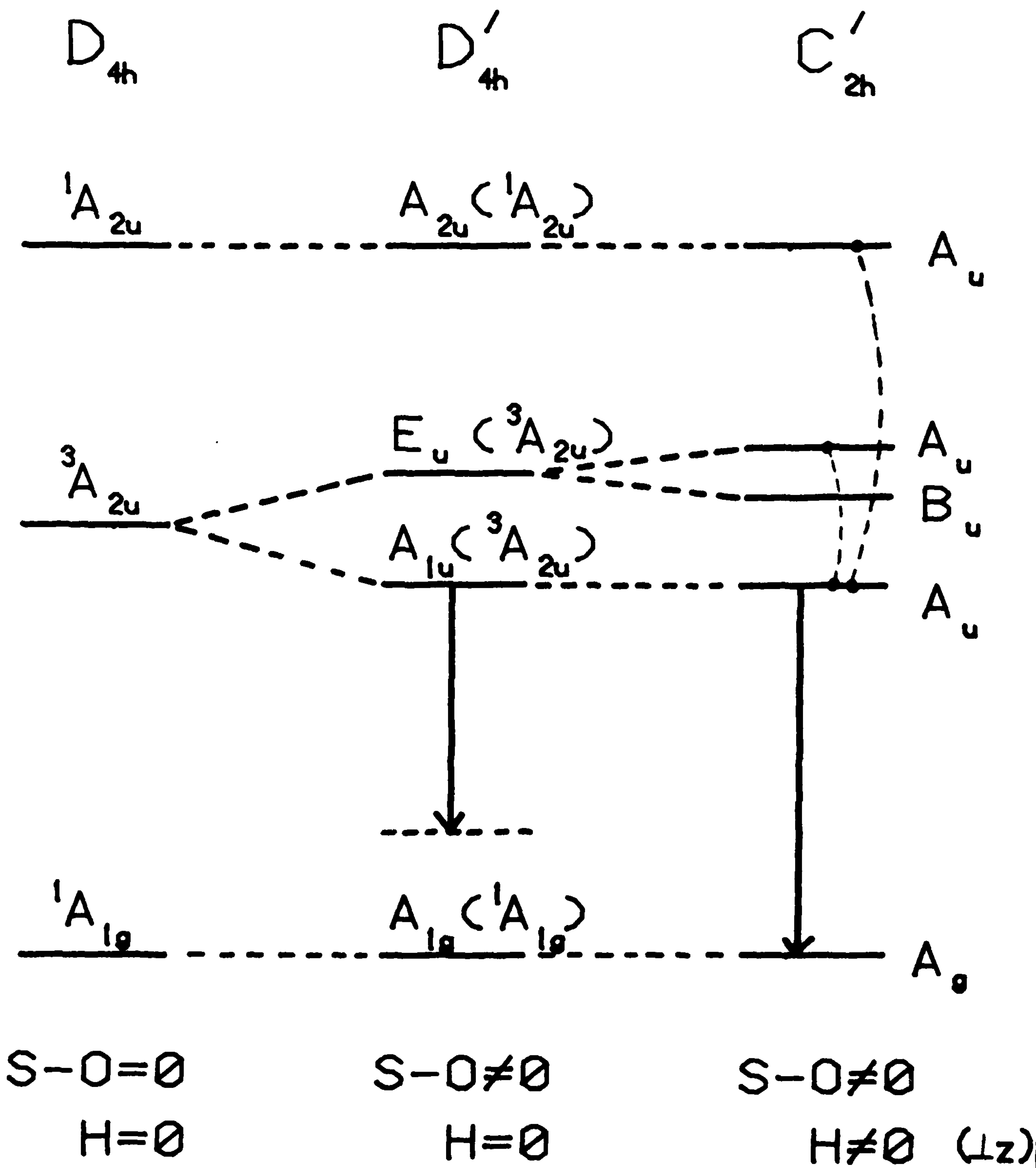


Fig 4



D_{4h}
D'_{4h}
C'_{2h}
$^1A_{2u}$
$A_{2u}(^1A_{2u})$
A_u
$E_u\ (^3A_{2u})$
A_u
$^3A_{2u}$
B_u
$A_{1u}(^3A_{2u})$
A_u
$^1A_{1g}$
$A_{1g}(^1A_{1g})$
A_g
S-O=0
S-O≠0
S-O≠0
H=0
H=0
H≠0 (⊥z)

Fig 5

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